NOV 26 1946

REGISTERED NO. M 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XXIV] *SECTION A* [NO. 3

SEPTEMBER, 1946

Price Rs. 2 or 3 Sh, *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

EQUILIBRIUM SURFACE TENSION OF AQUEOUS SOLUTIONS OF NEKAL BX AND THE EFFECT OF SALTS*

By T. Krishnappa, K. S. Gururaja Doss§ and Basrur Sanjiva Rao‖

Introduction

The study of the surface tension of aqueous solutions of wetting agents is of great interest from several points of view and has received considerable attention in recent years.[1,2] Wetting agents are so highly capillary active that they may be expected to form unimolecular adsorption film with a completely close packing, even at low concentration; this makes it possible to apply Gibbs' adsorption equation for the evaluation of the molecular cross-section. Since the molecular cross-section of these substances can also be investigated by spreading on aqueous substrates[3,4] a comparative study can be made of the two methods for the determination of cross-section. The study would be of interest in correlating wetting power with surface tension, for it is known that wetting power is intimately connected with surface tension.[5] Moreover wetting agents may be expected to show the phenomenon of activated accumulation discovered in this laboratory[6,7,8] and also independently by McBain and co-workers.[9,10] Surface tension studies can be expected to throw light on the interpretation of this phenomenon.

Experimental

Purification of Nekal BX

The main impurity in commercial Nekal BX is sodium sulphate. To remove this, Nekal BX was shaken well with hot benzene using a mechanical shaker. The undissolved portion was allowed to settle down. The supernatant solution was decanted out and the benzene was distilled off. The residue was dried, powdered, heated in an oven at 110° C. for six hours and stored in a stoppered bottle in a desiccator over dehydrated calcium chloride.

---

* Part of thesis submitted by T. K. in partial fulfilment of the requirements for the degree of Master of Science of the Mysore University.

§ Physical Chemist, Imperial Institute of Sugar Technology, Cawnpore.

‖ Principal, Central College, Bangalore.

Ash content of purified Nekal BX

A known weight of purified Nekal BX was ignited in a platinum crucible. The ash was treated with dilute sulphuric acid to convert it into the sulphate, and the excess of the acid was evaporated. The residue was ignited and weighed. The sodium content was found to correspond to 1·10 atoms of sodium per molecule of Nekal BX.

The osmotic coefficient of Nekal BX in aqueous solution at various concentrations

The osmotic coefficient was determined by the cryoscopic method and calculated using the formula

$$g = \frac{\theta}{\nu \lambda m},$$

where θ = depression of freezing point, $\nu = 2$, $\lambda = 1{\cdot}85$ and m = molal concentration of Nekal BX. If we assume that aggregation of only anions occurs and that the cations are all osmotically active, the average number of anions per micelle can be calculated. The values are given in Table I.

TABLE I

Concentration of Nekal BX g in 100 grams of water	θ	g	Average No. of anions aggregated to form a micelle
4·0	0·252	0·53	14·7
1·0	0·091	0·74	2·1
0·4	0·046	0·98	1·1
0·20	0·024	1·02	1·0

Preparation of flat springs of quartz

The surface tension was measured by the ring method. The determination of maximum pull was made by using a new type of silica spring prepared in the following manner. Silica fibre drawn in the usual way was attached to the steel blade of a spatula by means of a gummed label. Sharp bends were then given to the fibre at the edges of the spatula by heating with an oxy-gas flame. The blade was manipulated so as to get the fibres parallel to each other after each bend. After the winding was over the label was burnt off when the spring easily slid out of the spatula as the blade had a taper both in its width and in its thickness.

The springs that got are found to be very satisfactory. They obey Hooke's law perfectly. If from a fibre of given length, a helical spring

and a flat spring having same width are prepared, the two springs would give practically the same sensitiveness, as can be seen from the following considerations:—

The extension of a flat spring takes place by the bending of the fibres. The amount of extension x_1 can be calculated by the formula

x_1 = number of coils × displacement due to bending of each coil.

The displacement δ due to the bending of each coil can be calculated to a first approximation by considering it as equivalent to twice the displacement suffered by a horizontally cylindrical fibre fixed at one end when loaded at the other end. This is given by the equation,

$$\delta = \frac{2\,w\,d^3}{3\,Y\,A\,k^2},$$

where w = the load, d = width of the flat spring, Y = Young's modulus, A = cross-section of the fibre and k = radius of gyration[12].

$d = 2R$, where R is the radius of the spring whose diameter is equivalent to the width of flat spring.

$$A = \Pi r^2,$$

where r = radius of the cross-section of the fibre.

$$K^2 = \frac{r^2}{2}$$

$$\delta = \frac{32\,w\,R^3}{3\,Y\,\pi\,r^4}$$

Since the number of coils in the spring $= \frac{L}{4R}$, where L is the total length of the fibre,

$$x_1 = \frac{32\,w\,R^3}{3\,Y\,\pi\,r^4} \times \frac{L}{4\,R},$$

$$= \frac{8\,w\,R^2\,L}{3\,Y\,\pi\,r^4}.$$

For a helical spring of the total length L, radius R, the extension x_2 is given by the formula[12]

$$x_2 = \frac{2\,w\,R^2\,L}{n\,\pi\,r^4},$$

where n is the rigidity modulus.

Then,

$$\frac{x_1}{x_2} = \frac{4\,n}{3\,y}$$

For silica $n \cong 3$ and $y \cong 5$.

So, $$\frac{4n}{3y} = \frac{4 \times 3}{3 \times 5} = \frac{12}{15} = 0{\cdot}8,$$

showing that the sensitivenesses of the two types of springs are of the same order.

Flat springs can easily be prepared in less than half an hour while several hours have to be spent in the preparation of the helical springs even when an automatic device is employed.[11]

It has to be pointed out, however, that if the springs are to be enclosed in narrow tubes as in sorption work it is preferable to use the helical springs since the latter are more compact for any given sensitiveness and capacity.

Flat springs were prepared out of ordinary glass fibre but were found to be totally unsatisfactory. Even with pyrex glass small flow effects were noticed, especially when the springs were subjected to high loads for long intervals of time. The quartz springs however showed no detectable flow effects.

The quartz spring used in the present work had a sensitiveness of 2·7 cm. per gram. The travelling microscope used had an accuracy of 0·01 mm.

Temperature control

The ordinary air and water thermostats were found to be unsuitable for the work since the stirring arrangements caused too much disturbance of the surface and of the spring. The following arrangement was employed to overcome this difficulty. The conical flasks containing the solutions were kept in a shallow circular pan which contained water kept at 30° C. ± 0·1. Water from an electrically maintained thermostat 30° C. ± 0·1° C. was fed into the pan from four points symmetrically situated at the circumference of the pan. The level of the water in the pan was kept constant by pumping the excess of water back to the thermostat by means of a circulation pump. The suction tube for this purpose was kept at the centre of the pan. The chamber in which the experiment was tried was kept at 32° C. to 34° C. by keeping two heating mats in the chamber in suitable position in order to prevent the condensation of water on the sides of the flask containing the solution. The heating arrangement was also helpful in preventing a cooling of the water in the pan due to evaporation. Using this arrangement a constant temperature could be easily maintained for long periods without any special attention.

Determination of surface tension

The determination of equilibrium surface tension offers many difficulties. The method employed should be a static one, since the systems under consideration show surface aging. Of the static methods, the capillary rise method is defective on account of the friction effects that operate at the meniscus.[8] The sessile bubble and pendant drop methods are by far the best from this point of view though the technique has to be very elaborate to secure accurate results. The ring method is also found to be suitable for the purpose[13,14] and has been adopted in the present work. The conical flasks in which solutions were kept during the measurement of surface tension, were cleaned in the following manner:—

Flasks, whose rims had been ground, were treated with hot chromic acid mixture and then thoroughly cleaned with distilled water. They were next dried in an air oven at 140° to 150° C., cooled and again rinsed with distilled water taking care not to wet the outside of the flask. Surface-active impurities were thus eliminated. The flasks were once again dried and their necks were parafinned on the outside to eliminate any creeping in of surface-active impurities from the thermostatic bath. It was observed that unless these precautions were taken for avoiding contamination from surface-active impurities the results could not be reproduced. Except during the measurement of surface tension the flasks were kept covered with ground glass plates placed over the ground rims. A fresh surface of the solution was generated by running down the solution into the flask at a uniform rate by means of a fifty c.c. pipette at a position just touching the centre of the bottom of the flask. This is similar in principle to the method adopted by Alexander.[15] The flasks containing the solution were arranged in a circle at the circumference of the thermostatic pan mounted on a table which could be either rotated, raised or lowered. The rotatory movement was helpful in bringing one solution after another beneath the spring with minimum disturbance of the surface. The vertical movement of the table could be made very gently by a worm-gear arrangement and was employed in measuring the maximum pull. Movement of the spring to measure this pull was not practicable owing to the vibrations produced.

A Du Nouy ring fixed to a nichrome wire was flamed and attached to the spring which was suspended from a glass rod fixed to an iron stand. The spring had been previously calibrated. The knob of the hook of the spring was focussed through a travelling microscope and the corresponding reading was taken as the initial reading. The flask containing the solution whose surface had been freshly made, was brought underneath the ring. The ring was then completely dipped into the solution by pulling down the

nichrome wire with the fingers. On releasing the fingers the ring attached itself to the surface of the solution. The flask was then lowered and the position of the knob followed by adjusting the microscope until maximum pull was attained. It was possible to make this measurement without detaching the ring from the surface of the liquid. The values of the surface tension were obtained by applying the corrections indicated by Harkins and Jordan.[16] The following interpolation formula was derived from the data of Harkins and Jordan:

Surface tension $= 21{\cdot}6 + 117{\cdot}3\,(M - 0{\cdot}2) + 23{\cdot}75\,(M - 0{\cdot}2)^2$, where M is the maximum pull in grams. This holds for dilute aqueous solutions for Du Nouy ring $\left(\frac{R}{r} = 39{\cdot}0 \text{ and } R = 0{\cdot}636 \text{ cm.}\right)$ over a range of temperature 25° C. ± 15° C. The measurements were continued until equilibrium values were got and there was no significant change for at least one week. It was found necessary to continue the observation for about a month in order to get the final values. The equilibrium surface tension of solutions of Nekal BX in water, in 0·1 N sodium chloride, in 0·01 N sodium chloride, 0·01 N hydrochloric acid and 0·01 N sodium sulphate with different concentrations of Nekal BX were determined. The results are given in Tables II and III and Fig. 1.

TABLE II

− log C.	C = Wt. of Nekal Bx in 100 c.c. of water	Equilibrium surface tension		
		Soln. in water at 30° C.	Soln. in 0·01 N NaCl at 30° C.	Soln. in 0·1 NaCl (23° ± 2° C.)
3·0000	0·0010	71·2	..	..
2·6021	0·0025	65·1	..	51·1
2·3010	0·0050	60·8	57·6	46·6
2·0000	0·0100	56·3	53·0	41·6
1·6021	0·0250	50·0	46·8	36·2
1·3010	0·0500	46·2	41·7	31·9
1·0000	0·1000	41·0	37·7	29·9
0·6979	0·2000	36·3	33·3	29·3
0·3979	0·4000	31·9	31·6	29·3
0·2218	0·6000	..	..	29·6
0·0969	0·8000	31·5	31·3	29·8

TABLE III

g. Nekal BX in 100 g. water	Equilibrium surface tension		
	Soln. 0·01 N $BaCl_2$	Soln. in 0·01 N Na_2SO_4	Soln. in 0·01 N HCl
0·005	..	55·0	49·4
0·010	38·3	49·4	43·4
0·025	32·5	43·5	38·8

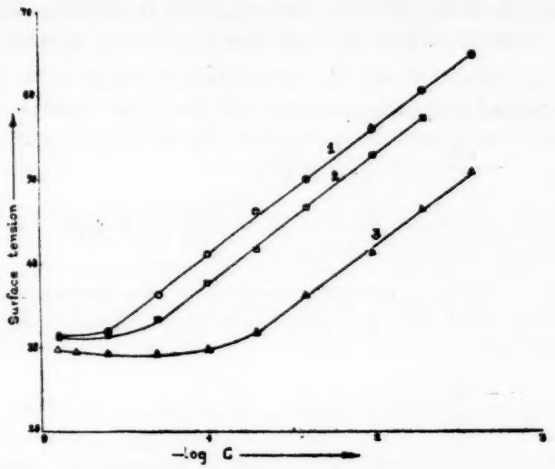


FIG. 1

Curve 1. Surface tension of Nekal B × Solution in water
Curve 2. ,, ,, ,, in 0·01N—NaCl
Curve 3. ,, ,, ,, in 0·1N—NaCl

DISCUSSION

1. *Application of Gibbs' adsorption equation.*

(i) ***The derivation of the usual form of Gibbs' adsorption equation.***—Gibbs derived[17] thermodynamically the important relation (for systems at constant temperature and pressure)

$$-d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_3 d\mu_3 + \ldots, \qquad (1)$$

where σ is the surface tension of a solution, Γ is the Gibbs' adsorption excess and μ the chemical potential. The subscripts 1, 2, 3, etc., refer to different components present in the solution. For a two-component system the equation becomes

$$-d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \ldots. \qquad (2)$$

Therefore,

$$-\frac{d\sigma}{d\mu_2} = \Gamma_1 \frac{d\mu_1}{d\mu_2} + \Gamma_2. \qquad (3)$$

But from the properties of partial molal quantities, we have,

$$N_1 d\mu_1 + N_2 d\mu_2 = 0, \qquad (4)$$

where N_1 and N_2 are mole fractions of the two components. Combining 3 and 4, we get,

$$-\frac{d\sigma}{d\mu_2} = -\Gamma_1 \frac{N_2}{N_1} + \Gamma_2. \qquad (5)$$

For any position of the dividing surface, if Γ_2 is positive, Γ_1 would be expected to be negative and would be proportional to Γ_2, so that one can put,

$$\Gamma_1 = -\alpha\Gamma_2. \tag{6}$$

Combining (5) and (6), we get,

$$-\frac{d\sigma}{d\mu_2} = \Gamma_2\left\{1+\alpha\frac{N_2}{N_1}\right\}. \tag{7}$$

It may be noted that α can be correlated with the relative dimensions of the two types of molecules, and is always positive.

Equation 7, which is perfectly general for two component systems can be further simplified for the particular case of dilute solutions. For if $N_1 >> N_2$ we get,

$$-\frac{d\sigma}{d\mu_2} = \Gamma_2. \tag{8}$$

Equation 8 represents the usual form in which Gibbs' adsorption equation is expressed and applies to all *dilute* solutions having two components, *irrespective of the position of the dividing surface.*

(ii) *Significance of the Gibbs' adsorption excess.*—Since equation (8) is true irrespective of the position of the dividing surface, one can put the dividing surface at the physical interface. Thus Γ_2 would give the amount of solute present in the adsorption layer in excess over what would have been present if there were no preferential adsorption of the solute. It may be pointed out that in *dilute solutions*, the quantities obtained by the moving bubble method[18] or by the highly exacting microtome technique[19] are identical with Γ_2.

(iii) *Nekal BX and type III curve.*—With pure Nekal BX solutions, neglecting activity coefficients, if the Gibbs' adsorption equation is applied, a unique behaviour is noticed. The adsorption increases with concentration, attains a constant value of $1{\cdot}60 \times 10^{14}$ moles. per sq. cm. and then abruptly falls to zero at a concentration of 0·4 per cent. Nekal BX. This corresponds to type III of McBain.[1] But the curve is very unique in one respect namely that the fall from maximum adsorption to zero adsorption is extremely steep.

Type III curve, as applied to Nekal BX, presents a paradox in the chemistry of surfaces as can be seen from the following considerations:—

(*a*) Gibbs' equation in the simplified form can be applied to this system as we are dealing with a dilute solution having a single solute. The Γ values give directly the amounts present in the surface layer.

(*b*) Whereas adsorption should increase with increase of concentration. it is found abruptly to fall to zero at a particular concentration.

(*c*) If it is to be assumed that the fall is due to micelle formation, the micelles being assumed to be surface-inactive, the question yet remains as to why the surface tension of the solution is so low when compared with that of water.

(*d*) The paradox cannot be attributed to any want of equilibrium since in each case ample time was allowed for equilibrium while the attainment of equilibrium was almost immediate at higher concentrations.

(*e*) Surface-active impurities have been avoided in measuring the surface tension, by taking the precautions detailed in the appropriate section.

(*f*) The microtome method as applied to analogous cause of lauryl sulphonic acid shows a positive adsorption in the region in which Gibbs' equation predicts a zero or a negative adsorption. (Such experiments however have not been carried out with Nekal BX.)

(*g*) The type of the curve remains unaltered even when the osmotic coefficients are taken into account while applying Gibbs' equation.

Attempts to explain this anomaly have been made by McBain[1] and by Alexander. McBain considers this problem in all its aspects and concludes that the Gibbs' adsorption equation itself is a limiting law. But it is not at all clear why it should be a limiting law. Alexander[2] seems to be right in his arguments in discarding the explanation of McBain, but his own explanation given to account for the curve is also unsatisfactory. Alexander considers that the whole complication is due to micelle formation. In applying the Gibbs' equation he considers the Gibbs' adsorption excess as made up of two parts: Γ_s (of single molecules) and Γ_m (of micelles). Then,

$$-d\sigma = \Gamma_w\, d\mu_w + \Gamma_s\, d\mu_s + \Gamma_m\, d\mu_m \qquad (1)$$

Placing the dividing surface so as $\Gamma_w = 0$ (and this is allowable in dilute solutions), we get,

$$-d\sigma = \Gamma_s^w\, d\mu_s + \Gamma_m^w\, d\mu_m \qquad (2)$$

If the single molecules and micelles are in equilibrium,

$$\mu_s = \mu_m \qquad (3)$$

whence

$$-d\sigma = \Gamma_s^w\, d\mu_s + \Gamma_w^m\, d\mu_s \qquad (4)$$

But

$$d\mu_s = \mathrm{RT}\, d\, ln\, c_s f_s \qquad (5)$$

where $c_s f_s$ is the activity of single molecules.

Combining 4 and 5,

$$-\frac{d\sigma}{dc} = RT\,(\Gamma_s^w + \Gamma_m^w)\,\frac{d\,c_s f_s}{dc}\cdot\frac{1}{c_s f_s}$$

Since $\frac{d\sigma}{dc} = 0$ [at higher concentrations], (c = total concentration of the solute)

either

$$\Gamma_s^w + \Gamma_m^w = 0 \tag{6}$$

or

$$\frac{d\,c_s f_s}{dc} = 0 \tag{7}$$

or

$$c_s f_s = \propto. \tag{8}$$

[Alexander puts the condition in equation (8) as $c_s f_s$ being equal to zero; but this is obviously a slip.]

Alexander considers that the condition in equation (7) is satisfied and not the others in order to explain the paradox.

The defect in the treatment of Alexander can be easily appreciated if one replaces equation (4) by its equivalent equation

$$-d\sigma = (\Gamma_s^w + \Gamma_m^w)\,d\mu_m \tag{9}$$

which, proceeding on lines similar to those adopted by Alexander, leads to the final conclusion

$$\frac{d\,c_m f_m}{dc} = 0.$$

It is not clear how this conclusion can be experimentally justified.

The defect in Alexander's argument appears to be in that it overlooks the important fact that Gibbs' treatment is thermodynamically rigorous and does not depend on any particular constitution of the solution. *Micelle formation is therefore a supernumerary phenomenon from the point of view of the application of Gibbs' adsorption equation.* As long as there is equilibrium between the micelles and the single molecules, it is unnecessary to separate either the activity or the Gibbs' adsorption excess of the single and polymer molecules. [Such a separation is tantamount to assuming single and polymer molecules as separate components; it would on the same lines be necessary to further increase the number of components taking into account the different polymers of water, the different hydrates of the solute, etc.] If the treatment is modified so as to remove this defect, the phenomenon of $\frac{d\sigma}{dc}$ becoming zero at higher concentrations, remains unexplained.

(iv) *Cross-section of Nekal BX molecule.*—If one can assume that Gibbs' adsorption equation can be successfully applied at concentration below that at which Γ becomes zero, one can show that the saturation of the surface occurs at a concentration of about 0·003 per cent. and the Γ remains constant at higher concentrations up to 0·4 per cent. of Nekal BX. The Γ corresponding to saturation $= 1{\cdot}60 \times 10^{14}$ molecules per sq. cm. $\therefore$ Cross-section = 62·5 sq. Å. The cross-section from surface film measurements[3] works out to be 53 sq. Å. The lower value in the latter case is probably due to the fact that barium chloride solution was used as the substrate.

It is of interest to note that the value of cross-section of Nekal BX at the surface of 0·01 N sodium chloride solution is almost the same (62·6 sq. Å) as that at the surface of water. But the cross-section got by calculating from the data obtained by working with Nekal BX solutions in 0·1 N sodium chloride works out to be 64·8 sq. Å, a value which is markedly higher. This result is rather surprising since addition of salts may normally be expected to reduce the electrostatic repulsion and consequently decrease the effective cross-section; but, the opposite has been found to be the case. This is presumably connected with the facts that (*a*) concentrations and not activities have been used in applying the Gibbs' equation and (*b*) with Nekal BX in 0·1 N sodium chloride, there is a three-component system.

2. *The theory of Cassie and Palmer*

Cassie and Palmer[20] have given an interesting theory for explaining the effect of salts on soluble, ionised monolayers and have brought in support of their theory, the data obtained by Powney and Addison.[21] An examination of the data on Nekal BX solutions (Tables II and III) shows that a divalent cation like the barium ion has much more effect than the univalent cation on the negatively charged monolayer. This observation is qualitatively in conformity with their theory.

A quantitative application however has given a different result. The values of λ^2 calculated according to equations (16·0) and (16·1) of Cassie and Palmer are given in Table IV. The results show that the value of λ^2 shows large variations unlike the corresponding values calculated from the data obtained by Powney and Addison. This shows that the theory of Cassie and Palmer is not valid in the present case. The disagreement is probably due to the wrong assumption made by Cassie and Palmer, that the surface pressure is a single valued function of Γ. That Γ need not be a single valued function of surface pressure is obvious from the work on the spreading of stearic acid on various substrates.[25] It is to be noted however, that this assumption is somewhat justifiable at high surface pressures

(for since the surface is closely packed the Γ values would not very much change with surface pressure). It is of interest to note in this connection that the data in Table IV tend to agree with the theory of Cassie and Palmer in the region of high surface pressure. The data of Powney and Addison, which are cited by Cassie and Palmer, also correspond to the same region. It is to be noted that H^+ ions bring about a much larger lowering of surface tension than Na^+ ions at an equivalent concentration. Though this is contrary to the simple considerations of Cassie and Palmer, it can be correlated with the well-known higher adsorbability of H^+ ions.[26] A quantitative examination of the effect of Ba^{++} ions has not been attempted since the theory breaks down even with 1 : 1 electrolytes.

The effect of salts on the equilibrium surface tension can be qualitatively interpreted in the following way. The equilibrium surface tension is governed mainly by the equilibrium concentration of the Nekal BX in the surface layer. The latter is determined by the rate of entry of the ions into the layer and the rate of escape of the ions into the bulk. The entry is checked by the electrical potential barrier due to the ionised monolayer.[8] The rate of escape into the bulk however would be comparatively unaffected by the electrical potential barrier. Addition of salt would increase the ionic strength of the solution and thereby lower the height of the potential barrier. This would increase the rate of entry of Nekal BX into the surface but would not affect the rate of escape into the bulk. The surface concentration would therefore get increased and the surface tension would get lowered. Ba^{++} ions could be expected to be much more effective than Na^+ ions since the former may directly attach themselves to the monolayer and reduce the electrical charge. The behaviour of sodium sulphate is of interest in this connection. Sodium sulphate is more effective than sodium chloride in reducing the surface tension at equivalent concentrations. This is presumably due to the fact that sodium sulphate solution has a higher ionic strength than sodium chloride solution of an equivalent concentration. It may be pointed out that the theory of Cassie and Palmer cannot account for this behaviour of sodium sulphate.

According to the theory of Cassie and Palmer,

$$\lambda^2 = \gamma_1 \cdot S_1 [S_1 + C_1] = \gamma_2 \cdot S_2 [S_2 + C_2],$$

where S_1 and S_2 are the concentrations of the surface-active electrolytes, C_1 and C_2 are the concentrations of the salt, and γ_1 and γ_2 are the activity coefficients of the corresponding solutions having the same surface tension. The values of λ^2 calculated from our data are given in Table IV and a survey of the table shows, as has been already pointed out, that the data tend to agree with their theory only at lowest surface tensions.

TABLE IV

Surface tension	Concentration of wetting agent in molarity*	Concentration of NaCl in molarity	Logarithm of activity coefficient	$\lambda^2 \times 10^8$
57·6	$2·53 \times 10^{-4}$	0·00	$\bar{1}·992$	6
	$1·59 \times 10^{-4}$	0·01	$\bar{1}·950$	145
53·0	$5·54 \times 10^{-4}$	0·00	$\bar{1}·988$	30
	$3·19 \times 10^{-4}$	0·01	$\bar{1}·949$	292
51·1	$7·47 \times 10^{-4}$	0·00	$\bar{1}·986$	54
	$4·20 \times 10^{-4}$	0·01	$\bar{1}·949$	388
	$7·96 \times 10^{-5}$	0·10	$\bar{1}·842$	554
46·6	$1·59 \times 10^{-3}$	0·00	$\bar{1}·980$	241
	$7·96 \times 10^{-4}$	0·01	$\bar{1}·948$	763
	$1·59 \times 10^{-4}$	0·10	$\bar{1}·842$	1106
41·6	$2·84 \times 10^{-3}$	0·00	$\bar{1}·973$	758
	$1·59 \times 10^{-3}$	0·01	$\bar{1}·946$	1629
	$3·19 \times 10^{-4}$	0·10	$\bar{1}·842$	2221
36·2	$6·37 \times 10^{-3}$	0·00	$\bar{1}·960$	3701
	$3·92 \times 10^{-3}$	0·01	$\bar{1}·941$	4756
	$7·96 \times 10^{-4}$	0·10	$\bar{1}·841$	5564

* Taken from the graph in Fig. 2.

3. *Application of Szyszkowski's equation*

For relating the surface tension of a solution with the concentration of the solute Szyszkowski[22] suggested empirically the equation

$$\frac{\sigma_0 - \sigma}{\sigma_0} = \mathrm{B} \log \left(\frac{c}{\mathrm{A}} + 1\right) \qquad (1)$$

where σ_0 and σ are the surface tensions of solvent and solution respectively. C is the concentration of the solute and A and B are constants. An examination of the Bond and Puls' treatment[23] of Szyszkowski's equation has shown that the latter can be justified on the basis of the Gibbs' adsorption equation and the Langmuir theory of adsorption. The following formal derivation can be given for Szyszkowski's equation:—

Number of molecules per sq. cm. in the surface layer in dilute solutions

$$= -\frac{1}{kT}\frac{d\sigma}{d\ln c} \tag{2}$$

Fraction of the total surface covered

$$= -\frac{1}{kT}\cdot\frac{d\sigma}{d\ln c}\,a, \tag{3}$$

where a is the cross-section of the solute molecule.

V_1 = rate of escape of molecules into the bulk

$$= -\frac{1}{kT}\cdot\frac{d\sigma}{d\ln c}\cdot K_1$$

V_2 = rate of arrival of molecules into the surface

$$= K_2 c\left\{1+\frac{1}{kT}\cdot\frac{d\sigma}{d\ln c}\,a\right\}$$

where K_1 and K_2 are constants.

At equilibrium $V_1 = V_2$. (4)

Solving the differential equation corresponding to equation (4), we get,

$$\frac{\sigma_0-\sigma}{\sigma_0} = \frac{kT}{a\sigma_0}\ln\left(1+\frac{K_2}{K_1}\,a\,c\right) \tag{5}$$

which is of same form as equation (1). Comparing (1) and (5), we get,

$$B = \frac{kT}{a\sigma_0} \text{ and } A = \frac{K_1}{K_{2a}}\cdot$$

It is easily seen that B is a function of a and therefore is constant for different members of the homologous series. A, however, would be proportional to K_1 and would therefore increase with decrease in chain length. This is again in agreement with Szyszkowski's observation.

Other merits of the equation are

(*a*) at low concentrations the solute can be shown to behave as a perfect gaseous film;

(*b*) at high concentrations the equation reduces itself to that of Milner[34] which is found to be in agreement with experimental results; and

(*c*) at the highest concentrations a limiting area is indicated.

An application of the equation to Nekal BX solutions shows that the equation is applicable up to 0·4 per cent. Nekal BX and then it breaks

down completely; this is because the Gibbs' adsorption equation itself does not apply beyond that concentration. (It is to be noted however that even the lowest concentrations of Nekal BX employed in the present investigation correspond to the formation of a practically complete unimolecular layer.)

4. *Micelle formation*

If the horizontal portion of the $\sigma - (-\log C)$ curves is interpreted as due to micelle formation, the concentration at which the micelle formation occurs may be taken as 0·4 per cent. in the case of pure Nekal BX solutions, and 0·27 per cent. in the case of Nekal BX solutions in 0·01 N-NaCl.

Summary

A simple technique has been described for the preparation of flat springs of quartz fibre. The new type of springs are found to be very satisfactory for the measurement of surface tension by the ring method.

A method for measuring the equilibrium surface tension of solutions (which show surface aging) has been described. Full details are given of the arrangement for adequate temperature control and for the prevention of contamination of solutions by surface-active impurities.

The equilibrium surface tension of Nekal BX solutions of various concentrations in water and in salt solutions, has been determined.

Application of Gibbs' equation to Nekal BX solutions has been discussed. Nekal BX solutions of concentrations above 0·4 per cent. have shown either no adsorption or negative adsorption, which cannot be explained on the basis of Gibbs' equation and the phenomenon therefore remains a paradox.

The arguments put forward by McBain and by Alexander to explain the type III curve have been shown to be untenable.

The cross-section of the Nekal BX molecule has been calculated on different substrates, *viz.*, water, 0·01 N and 0·1 N sodium chloride.

Applicability of Cassie and Palmer's theory to unimolecular adsorption layers formed by Nekal BX solutions has been discussed.

A formal derivation of the empirical equation of Szyszkowski has been given by combining Gibbs' equation and Langmuir's theory of adsorption and its application to Nekal BX solutions has been discussed.

References

1. McBain and Mills .. *Reports of Progress in Physics*, 1938, **5**, 30.
2. Alexander .. *Trans. Far. Soc.*, 1942, **38**, 248.
3. Venkatachala .. *Proc. First Annual Convention, Oil. Technologists' Association, India*, 1944, p. 11.
4. Krishnappa, Doos and Rao Unpublished.
5. Bhimasena Rao and Doss .. *Proc. Ind. Acad. Sci.*, 1941, **13**, 170.
6. Doss .. *Curr. Sci.*, 1935, **4**, 405.
7. ——— .. *Ibid.*, 1938, **7**, 182.
8. ——— .. *Colloid., Z.*, 1939, **86**, 205.
9. McBain and Wilson .. *J. Amer. Chem. Soc.*, 1936, **58**, 379.
10. ——— and Perry .. *Ind. Eng. Chem.*, 1939, **31**, 35.
11. Doss and Rao .. *Proc. Ind. Acad. Sci.*, 1936, **4**, 11.
12. Neuman and Searle .. *The General Properties of Matter*, 1936, 121, 127.
13. Nutting, Long and Harkins *J. Amer. Chem. Soc.*, 1940, **62**, 1496.
14. G. N. Subba Rao .. *M.Sc. Thesis*, Mysore University, 1942.
15. Alexander .. *Trans. Far. Soc.*, 1941, **38**, 15.
16. Harkins and Jordan .. *J. Amer. Chem. Soc.*, 1930, **52**, 1751.
17. Gibbs .. *Collected Works*, 1928, **1**.
18. McBain and co-workers .. *J. Amer. Chem. Soc.*, 1921, **49**, 2230; *ibid.*, 1929, **51**, 3534.
19. ——— and Swain .. *Proc. Roy. Soc.*, A, 1936, **154**, 608.
20. Cassie and Palmer .. *Trans. Far. Soc.*, 1941, **37**, 156.
21. Powney and Addison .. *Ibid.*, 1937, **33**, 1243.
22. Szyszkowski .. *Z. Physik. Chem.*, 1908, **64**, 385.
23. Bond and Puls .. *Phil. Mag.*, 1937, **24**, (7), 864.
24. *Cf.* Glasstone .. *Recent Advances in Physical Chemistry*, Second Edition, 1933, p. 325.
25. .. *Ibid.*, p. 335.
26. Doss .. *J. Indian Chem. Soc.*, 1933, **10**, 503.

AGING OF SURFACES OF SOLUTIONS

Part VI. Surface Aging of Casein Solutions*

By G. N. Subba Rao, K. S. Gururaja Doss† and Basrur Sanjiva Rao
(Department of Chemistry, Central College, Bangalore, S. India)

Received January 31, 1946

Introduction

Aqueous solutions of casein are known to produce foams of great stability. The foaming is due to the surface accumulation of the protein and the formation of adsorption films. These adsorption films are insoluble and exhibit surface pressure in the Langmuir trough. It is thus possible to study accumulation by the method developed by Doss[1] and independently by McBain and co-workers.[9, 10] Surface accumulation studies on casein are of particular interest since the area occupied by a casein molecule at the surface can be determined by direct spreading measurements. The surface aging of these solutions has been investigated in the present work by studying (*a*) the rate of accumulation and (*b*) the rate of change of surface tension with time. In studying the latter, a direct comparison has been made of the trough and the ring methods. The variation of surface tension has been studied by Johlin[6] by the capillary rise method. This method, however, is subject to many sources of error.[15]

Experimental

Casein used in the present work was an isodisperse fraction prepared according to the method of Svedberg, Carpenter and Carpenter.[13] The aging was studied by employing the surface film balance described previously.[2] The zero position of the float was adjusted to be vertically below the torsion wire so as to eliminate completely the effect of any changes in the vertical component of the force due to surface tension or buoyancy.[14] This is very necessary in the study of the variation of surface tension with time.

Results

1. *Accumulation studies.*—Casein has been found to accumulate very rapidly. It is therefore very necessary to work with a highly dilute solution

---

* Part of Thesis submitted by G. N. S. in partial fulfilment of the requirements for the degree of Master of Science of the Mysore University.

† Physical Chemist, Imperial Institute of Sugar Technology, Cawnpore.

in order to obtain a measurable rate of accumulation. 0·00025% solution in 0·01 M hydrochloric acid is found suitable.

The accumulated casein film is of a highly condensed type and it is therefore possible to measure the rate of accumulation by determining the area of the film. The rate of accumulation was measured as follows. The trough was thoroughly cleaned using Nekal BX which gave an extremely clear trough. A blank was invariably tried with distilled water before each study. The extent of contamination of a surface of distilled water was measured and found to be small, being invariably within 5% of the rate of accumulation of the casein solution. The trough was filled with the casein solution. The surfaces on either side of the float were swept clean by a barrier and the time noted. A known area of the surface on the left-hand side of the float was allowed to age for a definite amount of time and the area of the accumulated casein was measured at 4 dynes/cm. pressure by moving the barrier towards the float. At this pressure the force-area curve for spread films of casein was steep and hence area measurements were accurate. Since the area occupied by a molecular of casein at 4 dynes/cm. pressure was known from direct spreading, the rate of accumulation could be computed. The casein solution employed being exceedingly dilute, the process of accumulation impoverished the solution appreciably. This difficulty did not arise with the studies on benzopurpurine

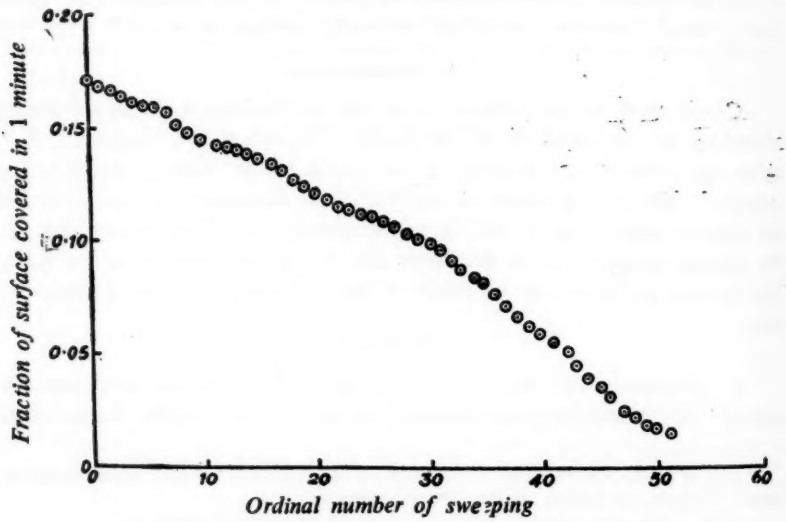


FIG. 1. Effect of repeated sweeping on the rate of accumulation of casein.

10 B since comparatively strong solutions (M/250, M/500) could be employed.[5] Fig. 1 illustrates this effect clearly. The successive one minute-values for the area covered with the same solution against the ordinal number of the sweepings have been plotted.

In order to get the time-area curve the following procedure was therefore adopted. For the value corresponding to each time-interval a fresh quantity of solution was started with. The surface was swept and accumulation measured thrice and the average of the three values taken. The results are given in Table I.

TABLE I

Time-area relationship to the accumulation of casein

0·00025 % casein in 0·01 M hydrochloric acid.

Area measured at 4 dynes/cm. Temperature 25° C.

Time in minutes	Fraction of the surface covered
1	0·17
2	0·26
4	0·38
8	0·59
16	0·83

The effect of salts on the rate of accumulation was studied and it was found that the rate of accumulation was not altered by the addition of potassium chloride or barium chloride.

The effect of temperature on the rate of accumulation was investigated. The trough was kept in a refrigerator at 13·5°C. It was found that the rate of accumulation was practically the same as at 25°C., the laboratory temperature. Attempts to measure accumulation at 40° C. were not successful owing to the serious disturbing effects caused by convection currents. Abnormally high accumulation was noticed—a 10° rise producing a twofold increases in the rate.

Accumulation of formolised casein.—Formolised casein was prepared by mixing solutions of Hammersten casein in aqueous sodium acetate with formaldehyde[8] and allowing to stand for three days. The rate of accumulation of 0·00025% solutions in 0·01 M-hydrochloric acid was studied. The results are given in Table II.

TABLE II

Time-area relationship relating to the accumulation of formolised casein

0·00025 % formolised casein in 0·01 M hydrochloric acid.
Area measured at 4 dynes/cm. Temperature 25° C.

Time in minutes	Fraction of the surface covered
1	0·092
2	0·12
4	0·16
8	0·26
16	0·33
32	0·46

2. *Variation of surface tension of casein solution with time.*—The variation of surface tension of casein solutions was studied by methods developed by Doss.[2] The reference surfaces used in the trough were (*a*) half-minute old and (*b*) fully aged. These methods correspond to procedures I and II independently developed by McBain.[10]

To start with, the trough was filled with the protein solution and the surfaces cleaned by barriers. The right-hand surface was always cleared half a minute before taking the readings for the pressure exerted by the aging surface on the other side. Thus the surface tension variation was measured using as reference the half-minute old surface. The measurements were

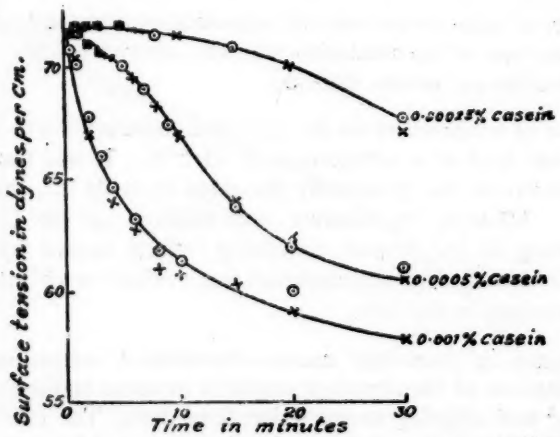


FIG. 2 Surface tension variation of casein solution in 0·01 M hydrochloric acid Temperature : 25°C. ⊙ Reference : half-minute old surface. × Reference : fully aged surface.

continued until a practically steady value was obtained. Then the surface on the right-hand side was cleared and allowed to age. The variation of surface tension of this surface was measured using the fully aged surface on the left as reference. The surface tension of the fully aged surface was then determined directly, by the ring method using the silica spring,[7] and the value employed in the calculation of the data given in Fig. 2.

When a fully aged surface was compressed (to 26 dynes/cm.), it exhibited a rise of surface tension on aging. The rise was about 5 dynes/cm. in ten minutes. The rise was steep initially and the behaviour was similar to that of benzopurpurine 6 B.[2]

A comparative study of the ring and trough methods was made, employing identical surfaces, and measuring the surface tension alternately by the two methods at various intervals of time. In the ring method a flat spiral of silica constructed in this Laboratory[7] was used for measuring the maximum pull. The results are illustrated in Fig. 3, and show that comparable results can be obtained by both the methods.

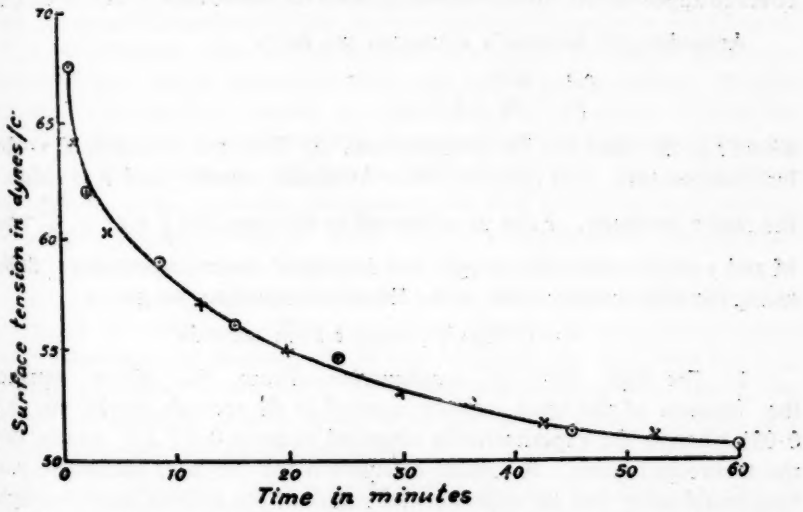


FIG. 3. Comparison of trough and ring method. ⊙ Ring method. × Trough method.

For 0·1% solutions, of casein, the trough method could not be used for studying the variation of surface tension since the solution wetted the paraffin and leakage past barriers occurred. The variation was therefore studied by the ring method. A two-minute old surface showed a surface

tension of 52·2 dynes/cm. Further aging caused a very slow change, the surface tension dropping to 50·8 dynes/cm. after one hour.

Discussion

1. *Calculation of the theoretical rate of accumulation.*—The order of time needed for covering any definite fraction of the total surface by accumulation can be estimated roughly as follows. For covering a fraction of the surface, the depth of the solution (below the surface) which is to be denuded $= \frac{\chi \times 10^{-7}}{2{\cdot}5 \times 10^{-6}}$ or 0·04 cm. (10^{-7} = No. of g. of casein present per sq. cm. of the casein monolayer at a pressure of 4 dynes/cm. on 0·01 M hydrochloric acid and $2{\cdot}5 \times 10^{-6}$ = concentration of casein in g. per c.c. of solution).

Consider the Brownian displacement of the molecules parallel to the vertical direction. Assuming that half the molecules move towards the surface by Brownian displacements, the distance Δ that a molecule has to cover to appear at the surface would be twice the above depth, *i.e.*, $0{\cdot}08\chi$ cm.

According to Einstein's equation, we have,

$$\frac{\Delta^2}{t} = \frac{RT}{N} \cdot \frac{1}{3\pi\eta r}$$

where t is the time for the displacement Δ, R = gas constant, T = absolute temperature, η = viscosity, N = Avogadro number and r = radius of the casein molecule. r can be estimated by the equation $\frac{4}{3}\pi r^3 = \frac{M}{\rho N}$ where M and ρ are the molecular weight and density of casein respectively. Substituting the appropriate values in the Einstein's equation, we get

$$\chi = 0{\cdot}012\sqrt{t}, \text{ where } t \text{ is in seconds.}$$

2. *The high rate of acculumation.*—From the above equation, the fraction of the total surface covered in 60 seconds works out to be 0·091 whereas the experimentally observed value is 0·17, *i.e.*, nearly twice the theoretical value. A similar calculation for the later successive intervals would show that the experimental values of the accumulation are higher than the maximum possible theoretical values. This is a surprising feature. All the systems studied so far by the earlier investigators[1, 11] exhibit slow accumulation. The abnormally high rate of accumulation now noticed cannot be explained on the basis of the presence in casein of any fractions of low molecular weight. For, the casein preparation used is known to be practically isodisperse. Moreover, to account for the observed high rate,

an average molecular weight of about 9,000 has to be assumed, a value which is obviously inadmissible. The observed high rate may at first sight appear to be caused by the dragging effect of the gegenions associated with the casein molecules. But the experiments on the effect of neutral salts definitely show that the influence of gegenions is negligible. It is of interest to note that a high rate of accumulation is not peculiar to casein. It is also exhibited by egg albumin.[12] Our observations suggest that this phenomenon is caused by (*a*) undulations produced during the formation of the new surface and (*b*) existence of eddy currents near the surface which disturb the concentration gradient set up by the diffusion of protein molecules into the surface.

3. *Effect of temperature on the rate of accumulation.*—The temperature coefficient of accumulation is negligible. The accumulation is therefore not activated. This observation supports the other fact that the accumulation is very fast.

As already stated, convection currents interfered with measurements attempted at 40° C. and gave very high values. Since the accumulation of casein is not of the activated type, any molecule of the protein reaching the surface by diffusion, sticks to the surface. Therefore the rate of accumulation is high and one is obliged to work with very dilute solutions. In such solutions accumulation causes a concentration gradient. Convection currents would disturb this gradient and promote diffusion, thereby increasing the rate of accumulation. It may be pointed out that this complication does not arise with systems like benzopurpurine 10 B giving activated accumulation,[2] for, the accumulation being slow no appreciable concentration gradient can occur in such system.

4. *Effect of neutral salts.*—Neutral salts have negligible influence on the rate of accumulation. This shows that there is no electrical potential barrier inhibiting accumulation.[15] It also confirms the view that the high rate of accumulation is not due to the influence of the gegenions, for, if they enhance the diffusion rate of casein molecules to the surface, neutral salts should reduce the rate of accumulation.

5. *The time-area curve.*—Langmuir's theory of adsorption can be applied to this system. The rate of increase of total surface covered by casein molecules is given by the equation

$$\frac{d\chi}{dt} = K_1(1 - \chi) - K_2\chi$$

where χ is the fraction of the total surface covered by casein molecules in a time-interval t, K_1, the specific velocity of adsorption and K_2 the velocity

of desorption. As the adsorption is practically irreversible K_2 may be taken as zero. (Actually K_2 may have a negative value. For, χ becomes unity when the surface pressure due to accumulation becomes 4 dynes/cm., the pressure at which the area of accumulated film is measured; but even at this stage accumulation continues, increasing the surface pressure much further.) The equation can then be written as

$$\frac{d\chi}{dt} = K_1 C (1-\chi) \text{ or } K_1 = \frac{1}{(t_1 - 1)} ln \frac{1-\chi_1}{1-\chi},$$

where χ_1 is the area covered in one minute. In Table III the values of K_1 for the accumulation of casein are given.

TABLE III

Accumulation of casein from 0·00025% *solution in* 0·01 *M hydrochloric acid*

t	K_1
2	0·050
4	0·042
8	0·044
16	0·046

In this discussion, the first minute value has not been taken into account owing to the disturbing factors that operate during the formation of a new surface. The examination of the table shows that the system obeys fairly well the Langmuir's equation. This shows that (*a*) the molecules of casein at the surface hinder accumulation of other casein molecules only to the extent of the surface they occupy at the surface pressure of 4 dynes/cm. and (*b*) the eddy current effects are nearly the same in all the measurements. A totally different result has been obtained with egg albumin[12] which does not obey Langmuir's equation. Molecules of albumin inhibit accumulation over an area about three times their cross-section. This is probably due to the influence of long-range electrical forces.

6. *Effect of formaldehyde.*—Accumulation of casein treated with formaldehyde shows a large diminution in the rate, if the fraction of total surface covered within a definite interval of time is considered. But taking into consideration the fact that the formolised casein occupies nearly half the area occupied by untreated casein, one finds the amount (in mg. per sq. m. of the surface) that has accumulated is nearly the same for the ordinary as well as the treated casein. This result shows that treatment with formaldehyde does not alter the state of aggregation of the molecule.

7. ***Variation of surface tension with time.***—The surface tension time curves for dilute solutions of casein can be interpreted, taking into account the condensed nature of the adsorption film. The accumulation starts, directly the new surface is formed. But accumulated molecules form a highly condensed film, having negligible surface vapour pressure. Consequently the surface tension remains constant though the accumulation proceeds. This goes on until the surface gets almost completely covered. At this stage further accumulation causes a large change in surface tension. At the next stage, when the surface gets highly packed up with molecules, the rate of penetration of casein molecules from the bulk solution into the surface decreases; so the slope of the surface tension-time curve decreases. In more concentrated solutions, accumulation goes on so rapidly that the initial horizontal portion of the curve is not noticeable. Similar behaviour has been noticed with solutions of lauric acid[16] and benzopurpurine 6 B.[4]

An examination of Fig. 2 shows that the values of surface tension are not so dependable when the fully aged surface is used as a reference surface. This is due to the fact that the surface tension of the fully aged surface is markedly upset by the irregular movements of the float during the determination.

When the adsorption film is compressed to a high pressure the surface tension of the compressed surface exhibits a rise in surface tension with time. This may be attributed either to a partial collapse of the film or to a change in the orientation of the molecules on the surface. With casein films, partial collapse has been noticed at a pressure of 26 dynes/cm.

Summary

1. The rate of accumulation of isodisperse casein has been investigated, employing a surface film balance. The rate is found to be much higher than the value expected from theory. This surprising feature, reported for the first time in the present work, has been explained.

2. Neutral salts have no effect on the rate of accumulation, thus showing the absence of influence of gegenions and of any electrical potential barrier.

3. Temperature coefficient of accumulation is negligible. Therefore the process is not activated.

4. Accumulation of formaldehyde-treated casein has been found to be essentially of the same order as of ordinary casein.

5. The time-area curve for casein obeys Langmuir's adsorption equation. There is no potential barrier inhibiting the accumulation.

6. Comparative study of the trough and ring methods for measuring surface tension has been made under identical conditions. The two methods are found to yield comparable results.

7. Variation of surface tension with time has been studied by the trough method.

References

1. Doss .. *Curr. Sci.*, 1935, **4**, 405.
2. ——— .. *Proc. Ind. Acad. Sci.*, A, 1936, **4**, 97.
3. ——— .. *Curr. Sci.*, 1937, **5**, 645.
4. ——— .. *Ibid.*, 1938, **7**, 182.
5. ——— .. *Kolloid-Z.*, 1938, **84**, 138.
6. Johlin .. *J. Phys. Chem.*, 1925. **29**, 271, 897.
7. Krishnappa, Doss and Rao .. Unpublished.
8. Lindstrom-Lang .. *Comp. rend. Lab. Carlsberg*, 1925, **16**, 48.
9. McBain and Wilson .. *J. Amer. Chem. Soc.*, 1936, **58**, 380.
10. ——— and Perry .. *Ind. Eng. Chem.*, 1939, **31**, 35.

11*a*. Nutting, Long and Harkins .. *J. Amer. Chem. Soc.*, 1940, **62**, 1500.

b. ——— and Long .. *Ibid.*, 1941, **63**, 87.

c. McBain, Ford and Mills .. *Ibid.*, 1940, **62**, 1324.

d. Ward and Tordai .. *Nature*, 1944, **154**, 146.

12. Rao, G. N. S., Doss and Rao, B. S. .. Unpublished.
13. Svedberg, Carpenter and Carpenter .. *J. Amer. Chem. Soc.*, 1930, **52**, 241.
14. Venkatachala, Doss and Rao .. Unpublished.
15. Doss .. *Kolloid-Z.*, 1939, **86**, 205.
16. Harkins and co-workers .. *Nature*, 1936, **138**, 406.

STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part V. Gel-Strength Measurements of Gels of Sodium Stearate in Pinene

By Mata Prasad, S. S. Dharmatti and G. S. Hattiangdi
(*Chemical Laboratories, Royal Institute of Science, Bombay*)

Received December 24, 1945

The gel-strength and modulus of elasticity have been considered to be an important and characteristic property of gels. The largest data available on the subject in literature is on gels of gelatin, probably because they are "rigid", and therefore it is easier to work with them than with gels of other substances which are comparatively "soft" and exude liquid and consequently lose their shape completely on an application of a slight stress.

An important investigation on the measurement of this property of gels in non-aqueous media has been carried out by Poole[1] in the case of cellulose acetate gels in benzyl alcohol. He finds that elasticity is approximately proportional to the square of the concentration, indicating that the rigid phase results from a dynamic solvation equilibrium between the cellulose acetate and the solvent. He proposes a Coefficient of Inner Resistance to denote the force which is required to produce unit velocity of "creep" (the increase in deformation with time when a steady stress is applied to a gel) in a unit cube of the gel in the absence of all elastic controlling forces. Lampitt and Money[2] also find that the gel-strength of gelatin gels is linearly related to the square of the concentration of the gel over a limited range.

In the present investigation the gel-strength of sodium stearate gels in pinene has been measured with a view to get some insight into the elastic properties of these soap gels in non-aqueous media. This soap was selected because it was found to give rise to stable and fairly stiff gels.

Experimental

The several methods which have been proposed for measuring or comparing the gel-strengths of gels may be divided into four main classes:

(*a*) dynamometer methods, in which the forces required to twist a column of the gel through definite angles are measured;

(*b*) methods involving the breaking of a gel;

(*c*) measurement of the depression produced by a constant load; and

(*d*) measurement of the load required to produce a definite depression. Soap gels in pinene are generally weak or "soft" for they lose shape and exude liquid on the application of a slight torsion. Hence dynamometric methods could not be employed to investigate the gel-strength of these gels.

Preliminary experiments made with a gel-testing apparatus similar to the one described by Oakes and Davis[3] showed that this method could be employed with advantage to measure the gel-strength of sodium stearate gels in pinene. In this apparatus, the bottom of one pan of a sensitive balance is attached to a plunger made of good quality glass. This is counterpoised so that the pointer rests at zero on the scale.

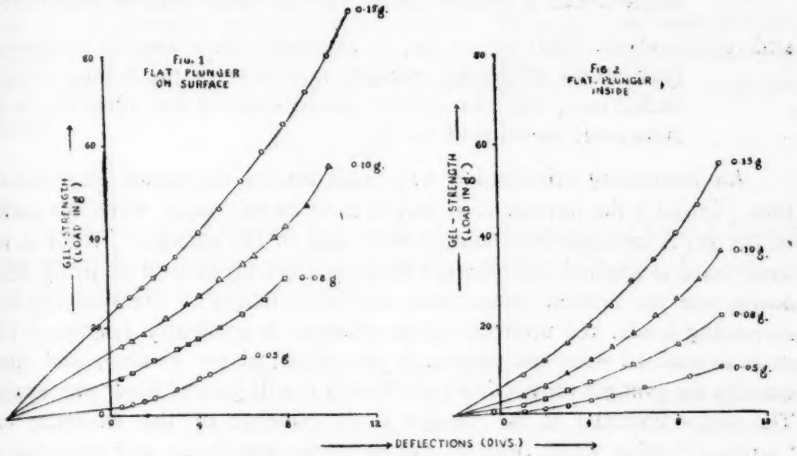
Gel-forming solutions containing varying amounts of sodium stearate (Merck's pure product) were prepared in 10 c.c. of pinene as described by Prasad and Hattiangdi[4] and were immediately poured into small weighing bottles in which they were allowed to set. The surface of the gel was then brought into contact with the plunger; weights were slowly added to the pan and the corresponding deflections on the scale as indicated by the pointer were noted. It was found that all small deflections of the pointer were proportional to the depression of the plunger. Such readings were taken till the breaking point or the elastic limit of the gel was reached. Care was taken to see that there was no jerking or oscillation of the plunger while in contact with the gel, and that the pressure was applied perpendicularly to the surface of the gel.

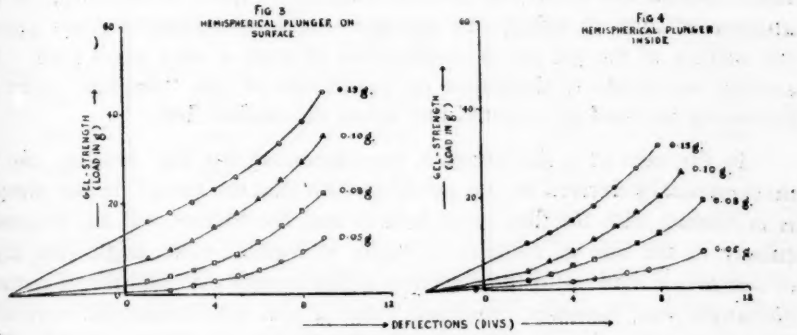
According to several earlier workers, all the methods which depend upon the breaking or compression of the gel in open glasses are subject to two sources of error: (*a*) the glasses usually vary in diameter thus forming a surface of variable area, and (*b*) there is always a "skin" of greater or less thickness which interferes with the accuracy of the test. The difficulty arising from the first cause was overcome by employing bottles of the same diameter ($2r = 2{\cdot}4$ cm.). To determine the existence, if any, of a "skin" or "surface" effect and the extent to which it vitiates the values of gel-strength, the plunger was dipped into a gel-forming solution before it was allowed to set; gel-strength measurements were carried out after the gel had set, in the same manner as described earlier.

Some workers recommend the use of a flat-ended plunger in preference to the hemispherically-ended one, since the area in contact with the gel is constant in the former case instead of increasing with depression as it happens if the latter type of plunger is used. In order that a comparison

of the two types of plungers could be made, a flat-ended circular disc-type plunger having a diameter equal to that of a hemispherically-ended one ($2r = 0{\cdot}8$ cm.) was prepared, and a series of load–deflection curves were obtained.

The various load-deflection results obtained for these gels are shown graphically in Figs. 1–4.





Discussion of Results

A comparison of the data obtained with the two types of plungers acting (i) on the surface of, and (ii) inside the gel, shows that

(*a*) both plungers give an almost linear loading curve until the elastic limit is exceeded;

(*b*) the deflection produced for a given load is much smaller in the case of a flat plunger than when the hemispherical plunger is used; this is due to the fact that the hemispherical plunger has a greater weight in proportion to the surface directly opposed to the gel, and is therefore better able to overcome the resistance of the gel. Thus the velocity of the hemispherical plunger is assisted and a greater range for the same load is obtained;

and (*c*) the elastic limit of the gel is reached with a smaller depression (deflection) of the flat plunger than that of the hemispherically-ended one; this is a direct consequence of the observation and behaviour mentioned in (*b*).

An interesting observation was made during the actual experimentation. Initially the pointer is at rest at zero on the scale when the surface of the gel is brought into contact with that of the plunger. When a very small load is applied, the plunger actually rises up instead of being forced down, and the pointer immediately starts oscillating. On applying small increasing loads, the upthrust of the plunger is gradually countered till a stage is reached when the pointer is once again at rest at zero, and subsequently the plunger moves downwards only if still greater loads are applied. The initial upthrust of the plunger is an evidence of the existence of a "surface" effect which behaves like an elastic membrane and whenever the loads applied are small the upward reaction is quite noticeable; in the absence of such an effect, the plunger would have pressed down against the surface of the gel on the application of even a very small load. An attempt was made to determine the magnitude of this "surface" effect by increasing the load till it could just break the surface film.

In the case of a flat plunger, the expression for the tension can be mathematically derived on the considerations that the rim of the flat plunger is in contact with the film to be broken and the tension will act perpendicularly to the line of contact. Usually in liquids, some angle (the angle of contact) is made with the direction of the tension and the line of contact. No angle was, however, observed when a rod was immersed vertically inside the gel, and hence the angle of contact was taken as zero. The total force acting upwards is therefore $2\pi r T_F$, where r is the radius of the plunger, and this is balanced by mg the force necessary to break the film. Therefore,

$$2\pi r T_F = mg,$$

or
$$T_F = mg/2\pi r. \qquad (I)$$

The expression in the case of the hemispherical plunger can be derived as follows. As increasing loads are applied, the plunger presses more and more against the surface of the gel, and near about the point when the skin is pierced the hemisphere is closely and completely surrounded by the membrane on the top of the gel. At this stage the extended membrane has an area $2\pi r^2$, where r is the radius of the sphere; the area of the membrane before this extension took place was only πr^2, and therefore the increase in area due to the action of the plunger is πr^2. Therefore the surface energy is equal to $\pi r^2 T_H$. This energy is derived by the work done by the weight mg in moving through a distance r, the buoyancy effect being neglected. Hence,

$$\pi r^2 T_H = mgr,$$

$$\text{or} \qquad T_H = mg/\pi r. \qquad \text{(II)}$$

The values of the tension T_F and T_H were calculated for gels of different concentrations of sodium stearate using the relations (I) and (II), and are given in columns 2 and 3 of Table I.

TABLE I

Values of the Surface Effect "T"

Soap content (in g.)	Determined from the limiting value of the load on the surface of the gel		Determined by the graphical method	
	Flat-ended plunger T_F	Hemispherical plunger T_H	Flat-ended plunger T_F'	Hemispherical plunger T_H'
0·05	1290	1169	2078	2027
0·08	3959	3945	4937	4755
0·10	6238	6238	6366	6239
0·15	8470	8055	8445	8420

The existence of the "surface" effect can be evidenced on different considerations altogether. If there were no such effect, the shear required to produce any strain should be the same wherever the plunger may be acting, on the surface or inside. The various curves in Figs. 1 and 2, and 3 and 4, however, show that the load required to produce a certain deflection is larger when either type of plunger is acting on the surface than when it is inside the gel. The difference between these two values of loads can be reasonably assumed to be the force which is necessary to counter the "surface" effect. The correctness of this assumption was verified by

determining the actual magnitude of the effect as follows. If L_1 is the load required to produce a certain deflection when the plunger is acting on the surface of the gel, and if L_2 is the load which produces the same deflection when the plunger is inside the gel, then $(L_1 - L_2)g$ is the force required to overcome the surface effect. Substituting $(L_1 - L_2)g$ for mg in equations (I) and (II), the values of T_F' and T_H' were calculated, and are given in columns 4 and 5 of Table I.

It will be seen from Table I that (i) there is a good agreement between the values of T_F and T_H and T_F' and T_H' over the range of concentrations studied, indicating that the value of T is almost independent of the nature of the plunger used, and (ii) there is a very good agreement between the values of T_F, T_H, T_F' and T_H' for 0·10 g. and 0·15 g. content of sodium stearate in the gel-systems, but the two sets of values are widely divergent for lower soap contents. The values obtained by the graphical method are higher than those obtained by the other method, but they are more correct for the following reasons. In the graphical method the value of m taken in calculating T for any concentration is the mean of several values computed from the graphs, while in the other method only one value of m can be available for calculation and a slight variation in the value of m would considerably affect the value of T. Hence the error is considerably minimised in the graphical method.

The development of a skin or membrane on the surface of the gel can be, in the first instance, very clearly seen when the gel-forming solution is being cooled. Further, it was observed that if the skin of a well-formed gel is pierced by a glass rod or plunger, the pierced portion of the surface appears like a fresh wound when the rod or plunger is withdrawn, and no fresh skin is formed on this spot even on keeping the gel for a sufficiently long time. This shows that a skin is formed during the process of setting of the gel. Its probable mode of formation is as follows. When a hot homogeneous solution of sodium stearate in pinene is allowed to cool, there is a rapid radiation of heat from the surface which brings about (i) an immediate inhomogeneity in the distribution of the solute in the dispersion medium, and (ii) a quick evaporation of the pinene due to which a semi-dry skin or membrane is formed on the surface of the gel. The skin or membrane is thus formed only during the process of setting of the gel, and not at any stage afterwards.

Previous workers have shown that Hooke's law holds true in the case of gels, that is the load–displacement curve is a straight line passing through the origin, and its slope is proportional to elasticity. The earlier portions

of the curves in Figs. 1–4 are straight lines, thus showing that Hooke's law is obeyed up to certain loads only; but with increasing loads these lines bend into a curve which shows that the elastic limit or the fatigue point has been exceeded. If the straight lines are produced backwards, they do not meet at the origin but some point which may be taken as the true origin of the load-deflection co-ordinates. The shape of these curves and the abovementioned behaviour are similar to those reported by Oakes and Davis[3] and Sheppard and Sweet[5] in the case of gelatin gels, using similar plunger methods. The difference in the nature of the earlier portions of the curves in the soap–pinene systems and gelatin gels may be caused by the varying surface of contact of the plunger employed in the latter case.

The gel-strength can be measured either from the slope of the straight lines which converge to a point, or by comparing the loads required for the same deflection. The values of gel-strength were calculated from the slopes of the load–deflection curves shown in Figs. 2 and 4, that is, when the plunger is placed inside the gel, and are given in the following table.

TABLE II.

Values of Gel-Strength (arbitrary units)

Soap content (in g.)	Flat-ended plunger	Hemispherical plunger
0·05	0·75	0·75
0·08	1·75	1·50
0·10	2·75	2·20
0·15	3·75	2·80

The above results show that the gel-strength increases as the soap content of the gels is increased; the slight variation in the actual values when the two types of plungers are used is mainly due to the fact that when the hemispherical plunger is acting, the micelles get more opportunity to orientate themselves in such a way as to reduce the resistance and to increase the strain, and hence the gel-strength values are slightly smaller. Although it is an anomaly to say that a physical property like elasticity is different when different methods are used, it is not surprising to find such a behaviour in these gel systems where the binding forces between the micelles are of such a small order as could be destroyed by mere mechanical agitation.

Poole and others have found that the plots of the logarithm of elasticity or gel-strength (E) against the logarithm of the concentration (C) are approximately straight lines in several cases, and the value of the slope does not

exceed 2. On plotting the values of log E against log C, obtained from the data given in Table II, it was found that the several points lie very nearly on a straight line whose slope is equal to 1·8 which closely approximates to 2. This observation is in accordance with the fibrillar theory of gel-structure developed by Poole. It has, however, to be remarked that the variation of elasticity or gel-strength as the square of the concentration, according to the theory, does not appear to hold true in the case of soap-pinene systems for higher concentrations.

One of the authors (G. S. H.) is grateful to the authorities of the University of Bombay for awarding him a University Research Scholarship, which has enabled him to carry out this investigation.

Summary

The gel-strength of gels of sodium stearate in pinene has been measured by the plunger method under several conditions. The values of elasticity have been calculated from the load–deflection curves, and it is found that log E varies linearly as log C, the slope of this straight line being very nearly equal to 2. The existence of a skin or membrane on the surface of the gel which vitiates the values of gel-strength has been critically examined, and its approximate magnitude has been determined.

References

1. Poole .. *Trans. Farad. Soc*, 1925, **21**, 114.
2. Lampitt and Money .. *J. Soc. Chem. Ind.*, 1936, **55**, 88 T.
3. Oakes and Davis .. *J. Ind. Eng. Chem.*, 1922, **14**, 706.
4. Prasad and Hattiangdi .. *Proc. Ind. Acad. Sci.*, 1945, **21**, 1.
5. Sheppard and Sweet .. *J. Ind. Eng. Chem.*, 1923, **15**, 571.

STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part VI. Viscosity Changes with Time and Shear during the Gelation of Some Soap Systems in Pinene

BY G. S. HATTIANGDI AND S. P. ADARKAR

(Chemical Laboratories, Royal Institute of Science, Bombay)

Received December 24, 1945

(Communicated by Dr. Mata Prasad, F.A.SC.)

IN a recent communication, Prasad and co-workers[1] have determined the viscosity changes that take place during the setting of solutions of sodium oleate and sodium stearate in pinene when they are cooled to different temperatures, using two types of viscometers, namely, the capillary-type Ostwald viscometer and the Falling Sphere viscometer. The regularities observed in the viscosity data obtained by the latter instrument during the process of gel-formation could, according to them, be expressed by the empirical relation $\eta - \eta_0 = ae^{kt}$, whereas the data obtained with the capillary viscometer obeyed the well-known Einstein's equation $\eta/\eta_0 = 1 + k\phi$ within a certain range of temperature only. It is very important to determine the effect of shear on the viscosity values obtained during the sol-gel transformation. An attempt in this direction was made in the case of cellulose acetate gel-forming systems in benzyl alcohol by Mardles[2] who observed that the values of the apparent viscosity decrease with increasing shear, and the nature of the viscosity-time curve changes its character with a change in the shear applied. He has, however, given no satisfactory explanation for this peculiar behaviour of the gelating systems.

This investigation gives the results of the measurements of the viscosity changes with time of some soap systems in pinene during the process of setting when different shears are applied. The soaps used are sodium oleate, sodium stearate and sodium palmitate, and the viscosity determinations have been made by employing a rotating cylinder viscometer.

EXPERIMENTAL

The sodium oleate and sodium palmitate used were products of the B. D. House, and sodium stearate of Messrs. E. Merck. The pinene used was obtained from Messrs. Eastman Kodak & Co., and was the fraction distilling at 156°.

The rotating cylinder viscometer used was manufactured by Messrs. W. G. Pye & Co., and consisted of a hollow cylinder (3·73 cm. in diameter and 10 cm. in length), which was rotated in a cylindrical vessel containing the gel-forming solution, there being a clearance of 0·678 cm. between the walls of the two cylinders. The inner cylinder was rotated by means of falling weights attached to the ends of a thin tough cord which passed over frictionless pulleys. The effective radius of the drum, D, round which the cord was wound was 1·91 cm. The value of the viscosity was calculated from the relation

$$\eta = \frac{g\,D\,(a^2 - b^2)}{8\,\pi^2 a^2 b^2} \cdot \frac{MT}{l + k}.$$

TABLE I

Sodium oleate in pinene

Soap content (in g.)	Time interval (in mts.)	Relative viscosity values at different rates of shear		
		10 g.	15 g.	20 g.
0·60	0	2·50	2·50	2·50
	1	2·60	2·55	2·55
	2	2·80	2·70	2·65
	3	3·25	2·93	2·84
	4	3·69	3·06	3·02
	5	3·89	3·45	3·20
	10	do	3·73	3·56
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do
0·75	0	3·10	3·10	3·10
	1	3·40	3·25	3·20
	2	3·85	3·45	3·30
	3	4·50	3·70	3·45
	4	4·99	3·85	3·60
	5	5·29	4·00	3·73
	10	5·58	4·35	4·14
	20	do	do	4·35
	30	do	do	do
	40	do	do	do
	50	do	do	do
0·90	0	4·15	4·15	4·15
	1	4·43	4·27	4·21
	2	4·65	4·40	4·27
	3	4·98	4·65	4·36
	4	5·10	4·95	4·62
	5	5·32	5·07	4·75
	10	5·84	5·33	5·00
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do

The radius of the outer and inner cylinders, *a* and *b*, were 2·543 cm. and 1·865 cm., respectively; M is the mass applied to the end of the cord and is proportional to shear; T is the time taken (in seconds) for one complete revolution of the cylinder; *l* is the length of the gel, and *k* the constant of the instrument ($k = 0 \cdot 55$).

The solutions of the various sodium soaps in pinene were prepared by dissolving known amounts of the soap in 60 c.c. of pinene as described by Prasad and Hattiangdi[3]; the results of the various experiments are given in Tables I to III.

TABLE II

Sodium stearate in pinene

Soap content (in g.)	Time interval (in mts.)	Relative viscosity value at different rates of shear						
		10 g.	15 g.	20 g.	30 g.	40 g.	50 g.	60 g.
0·60	0	3·0	3·0	3·0	3·0	3·0	3·0	3·0
	1	3·34	3·20	3·1	3·07	3·06	3·06	3·05
	2	3·57	3·51	3·25	3·15	3·12	3·08	do
	3	3·81	3·70	3·4	3·25	3·17	3·1	do
	4	3·96	4·12	3·6	3·33	3·20	3·1	do
	5	4·12	do	3·75	3·42	3·25	3·15	do
	10	4·46	do	3·9	3·64	3·50	3·25	do
	20	4·95	do	do	do	do	do	do
	30	do	do	do	do	do	do	do
	40	do	do	do	do	do	do	do
	50	do	do	do	do	do	do	do
0·75	0	4·2	4·2	4·2	4·2	4·2	4·2	4·2
	1	4·44	4·35	4·33	4·32	4·31	4·3	4·2
	2	4·7	4·55	4·5	4·45	4·33	4·3	4·3
	3	4·95	4·8	4·75	4·64	4·45	4·41	do
	4	5·60	5·2	4·98	4·8	4·55	4·45	do
	5	6·19	5·5	5·25	4·9	4·65	4·5	do
	10	8·42	6·91	6·25	5·52	5·0	4·8	do
	20	8·91	7·76	6·6	do	do	do	do
	30	do	do	do	do	do	do	do
	40	do	do	do	do	do	do	do
	50	do	do	do	do	do	do	do
0·90	0	5·0	5·0	5·0	5·0	5·0	5·0	5·0
	1	5·25	5·15	5·07	5·06	5·06	5·06	5·06
	2	5·59	5·32	5·25	5·11	5·11	5·06	do
	3	6·0	5·54	5·32	5·24	5·15	..	do
	4	6·52	5·8	5·53	5·32	5·2	5·1	do
	5	6·75	6·25	5·71	5·45	5·25	5·2	do
	10	8·69	7·58	6·95	5·95	5·50	5·25	dn
	20	do	do	do	do	do	do	do
	30	do	do	do	do	do	do	do
	40	do	do	do	do	do	do	do
	50	do	do	do	do	do	do	do

TABLE III

Sodium palmitate in pinene

Soap content (in g.)	Time interval (in mts.)	Relative viscosity values at different rates of shear		
		10 g.	15 g,	20 g.
0·60	0	2·6	2·6	2·6
	1	2·8	2·8	2·69
	2	3·1	3·0	2·90
	3	3·42	3·3	3·05
	4	3·8	3·5	3·31
	5	4·25	3·6	3·45
	10	5·1	4·0	3·7
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do
0·75	0	3·5	3·5	3·5
	1	3·6	3·57	3·55
	2	3·99	3·7	3·65
	3	4·5	3·99	3·87
	4	4·85	4·2	4·00
	5	5·05	4·32	4·1
	10	5·51	4·65	4·35
	20	5·82	5·45	do
	30	do	do	do
	40	do	do	do
	50	do	do	do
0·90	0	5·25	5·25	5·25
	1	5·38	5·35	5·30
	2	5·6	5·45	5·35
	3	5·9	5·58	5·45
	4	6·15	5·76	5·55
	5	6·31	5·95	5·70
	10	6·6	6·26	5·95
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do

DISCUSSION OF RESULTS

The effect of shear on the viscosity changes during gelation is very pronounced. The viscosity values decrease with an increasing shear, and the shape of the viscosity–time curves of the same system under different shears goes on changing. As a typical case the decrease in the apparent viscosity value with increasing shear for the gelating system of sodium stearate in pinene (0·75 g. in 60 c.c.) is shown by means of curves in Fig. 1. It will be observed from these curves that for low shears (10 g. to 30 g.) the viscosity-time curves rise slowly at first and then rapidly till they tend to run almost parallel to the viscosity axis; this is the condition when the setting

point is being approached. After this stage the curve takes a sudden turn and runs parallel to the time axis, indicating that the values of viscosity remain constant for any given set of experimental conditions. These curves would therefore appear to be different from those obtained by Prasad, Hattiangdi and Vishvanath[1] in the sense that the last part of the curves parallel to the time axis is absent. This is due to the fact that when the gel is set, there is no longer any velocity gradient in the gel, and the only consequence of the applied shear is a sort of slipping between the outer surface of the inner cylinder and the surface of the gel in contact with it.

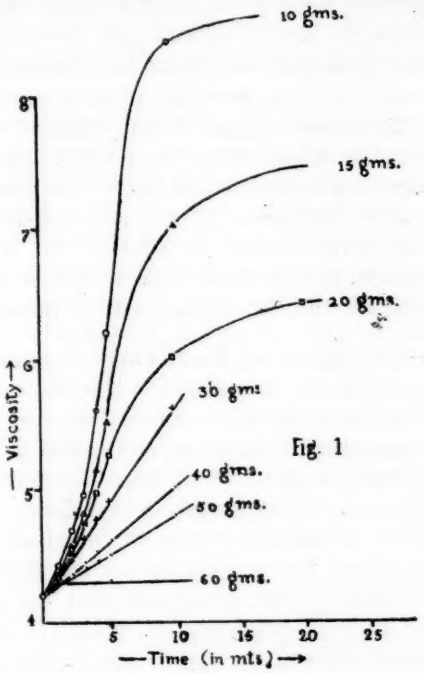


Fig. 1

This slipping is of a similar nature as that of rolling friction and has the same value as the viscosity of the set gel. As the shear is slowly increased, it is found that the apparently S-shaped nature of the curve is maintained, that is, the top part of the curve runs parallel to the time axis due to the constant value of viscosity attained by the gel system. For high rates of shear, however, the viscosity increases linearly with time and then reaches an almost constant value, the position of the straight lines moving towards the time axis as the shear is increased. The results obtained by Mardles[8] are similar

to these observations. The peculiar phenomenon of anomalous viscosity exhibited by the soap systems during gel-formation can be explained on the basis of the mechanism of the formation of these gels stressed by Prasad and co-workers in a number of papers. According to them, gel-formation results from (i) the gradual increase in the number and size (volume) of the soap micelles which are aggregates of small soap particles, (ii) the solvation of these micelles with the dispersion medium which is a saturated solution of soap in pinene, (iii) the fusion or aggregation of these solvated micelles into fibrils, and (iv) the enclosure of the intermicellary fluid in the interfibrillar space in an adsorbed state due to the attractive or linking forces between the fibrils. Prasad and co-workers have also shown that all the aforesaid processes take place simultaneously in the gel-forming system although some of them may take place preponderantly at one time than the others. Thus when a gel-forming solution of soap in pinene is allowed to cool to a low temperature, there will firstly be, preferably on an average, an increase in the number and size of the micelles and this will be abundantly followed by processes (ii), (iii) and (iv) described above. As a consequence, in the earlier stages of gelation, the structural gel-strength which is linked with the growth of the micelles will be weak and will become stronger as time elapses and the setting point is being approached.

The viscosity–time curves (*cf.* Fig. 1) for low rates of shear bring out the above-mentioned points very clearly. The slow increase in viscosity initially is caused by the increase in the number and the size of the soap micelles; the subsequent fairly rapid rise shows that the increase in viscosity with time is considerably accelerated owing to the large degree of solvation of the soap micelles and their aggregation into fibrils. The very rapid rise in viscosity during the last stage is due to the formation of a structure in the gel which behaves almost like a solid and hence offers a great resistance. These observations lead to the conclusion that the aforesaid behaviour would be shown by the gel-forming systems of soap in pinene if a viscosity-time curve is obtained without the application of any shear (*cf.* the curves obtained by Prasad and others[1]).

When the viscosity measurements are made with these gel-forming systems under different shear, two processes take place simultaneously, namely, (i) the occurrence of the processes described above, and (ii) the breakdown of all or some of the functions in the processes due to the shear acting in a direction opposite to the forces which come into play during the gel-formation.

The S-shaped curves obtained with increasing shear varying from 10 g. to 30 g. show that excepting for the earlier portions, the curves are lowered on increasing the shear, the latter part being lowered more than the earlier one. This shows that the application of the shear causes a general decrease in the rates of the occurrence of the four processes involved in gel-formation of soap-pinene systems, and the decrease is considerably more in the last three processes than the first one. This means that there is not only a decrease in the number and volume of the micelles formed owing to the application of the shear but their extent of solvation and aggregation into fibrils is also decreased, and hence the formation of a structure which causes a gel to set is delayed. This view is supported by the fact that the gel takes slightly more time to set when the shear applied is increased from 10 g. to 30 g.

When the shear is increased to 40 g. and 50 g., it is observed that (i) the viscosity–time curve is a straight line, that is, the acceleration in viscosity entirely disappears, and (ii) the earlier parts of the curves in the two cases are practically coincident. On the basis of the theory outlined above it means that factors which tend to form the essential agents for the formation of gel-structure are prevented from getting into action by the opposing shear. Since the gradients of these straight lines are less than those of the earlier parts of the curves for 10 g. to 30 g., it appears that the increase in viscosity at uniform rate in these two cases takes place mostly owing to the constant rate of increase in the number and the size of the micelles, and possibly, to some extent, to their solvation. This view is supported by the fact that when shears higher than 30 g. are applied, the system does not set to a gel even on keeping it for a sufficiently long time after the application of the shear, probably because the structure has been very badly broken down, and it looks like a suspension of soap in pinene.

On further increasing the shear to 60 g., the viscosity increases slightly in the beginning (during the first one or two minutes) and then attains a constant value. This shows that initially some micelles are formed which give the observed viscosity value to the gel-forming system; later on, the application of the high shear either destroys or prevents completely (i) the formation of more micelles and (ii) their increase either in volume, solvation, or aggregation. The viscosity–time curve for 60 g. of shear therefore represents the condition of the formation of a minimum number of micelles in this particular instance which is not affected by the shear.

This discussion leads us to two important conclusions regarding the application of shear, namely, (i) it can prevent or destroy the formation of gel structure which is responsible for the acceleration of viscosity with time,

and (ii) it can also decrease the rate of formation of the micelles or of the increase in their size or degree of solvation.

According to Goodeve and Whitefield[4], there is an equilibrium under certain conditions of steady shear between the rate of increase of the concentration of the micelles in a thixotropic system and their breakdown, and the apparent viscosity η of the system is given by the relation

$$\eta - \eta_0 = \frac{\theta}{s},$$

where η_0 is the residual viscosity, s the shear, and θ the coefficient of thixotropy. They also report that on plotting the observed values of viscosity against the reciprocal of shear straight lines are obtained. According to Freundlich, Goodeve and others, thixotropy indicates the isothermal decrease of viscosity with increase in rate of shear. In the light of the above definition, soap gels in pinene may be considered to be thixotropic and hence may conform to the above mentioned relation. This has been found to be so. On plotting the values of the apparent viscosity (η) against the reciprocal of the shear $\left(\frac{1}{s}\right)$, the curves obtained are straight lines for all the gel-forming systems studied in this investigation. Further according to the relation given above, the intercepts of the straight lines on the viscosity axis must be equal to η_0, the residual viscosity of the system. The values of η_0 have been determined and have been found to correspond to the state of the soap-pinene systems upto which all the $\eta - t$ curves are coincident. The residual viscosity may therefore be interpreted as the true viscosity of the colloidal system containing soap micelles which have undergone little or no solvation. Acccording to the considerations brought out in the discussion, this part of the viscosity–time curves corresponds to the soap-pinene system which contains practically only the soap micelles in a colloidal state in pinene.

The authors are extremely grateful to Dr. Mata Prasad, D.Sc., F.I.C., and Dr. S. S. Dharmatti, PH.D., F.INST.P., for the kind interest they took while this work was under progress; one of the authors (G. S. H.) is grateful to the authorities of the University of Bombay for awarding him a University Research Scholarship.

SUMMARY

Measurements of the viscosity changes with time taking place in the gel-forming systems of certain soaps in pinene yield $\eta - t$ curves which change their shape considerably as the shear applied is varied. It is also found that the shear applied can (i) prevent or destroy the formation of a gel structure which is responsible for the acceleration of viscosity with time,

and (ii) decrease the rate of formation of the micelles or of the increase in their size or degree of solvation. The plots of viscosity against the reciprocal of the shear are straight lines, indicating that the equation $\eta - \eta_0 = \theta/s$ is applicable to these soap-pinene systems.

References

1. Prasad, Hattiangdi and Vishvanath .. *Proc. Ind. Acad. Sci.*, 1945, **21**, 90.
2. Mardles .. *Trans. Farad. Soc.*, 1923, **18**, 327.
3. Prasad and Hattiangdi .. *Proc. Ind. Acad. Sci.*, 1945, **21**, 1.
4. Goodeve and Whitefield .. *Trans. Farad. Soc.*, 1938, **34**, 511.

668-46. Printed at The Bangalore Press Bangalore City, by G. Srinivasa Rao, Superintendent,
and Published by The Indian Academy of Sciences, Bangalore